

TEAR RESISTANT ELASTIC CRYSTAL GELS SUITABLE FOR
INFLATABLE RESTRAINT CUSHIONS AND OTHER USES

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RELATED APPLICATIONS

This application is a continuation-in-part of the following applications: U.S. Serial Nos: 08/984,459, filed 12/3/97; 08/909,487, filed 7/12/97; 08/863,794, filed 5/27/97; 08/819,675 filed March 17, 1997; PCT/US97/17534, filed 30 September 1997; U.S. Serial No: 08/719,817 filed September 30, 1996, U.S. Serial No: 08/665,343 filed June 17, 1996 which is a Continuation-in-part of U.S. Serial No: 612,586 filed March 8, 1996 ~~which is a Continuation-in-part of Serial Nos: 705,096 filed 5/23/91, 152,735 filed 11/15/93, 152,734 filed 11/15/93;~~ PCT/US94/04278 filed 4/19/94 (published 5/26/95 No. WO95/13851); PCT/US94/07314 filed 6/27/94 (published 1/4/96 No. WO 96/00118); 288,690 filed 8/11/94; 581,188 filed 12/29/95; 581,191 filed 12/29/95; 581,125 filed 12/29/95. In turn U.S. Serial Nos. 581,188; 581,191; and 581,125 are continuation-in-parts of the following applications: Serial Nos.: 288,690, filed August 11, 1994, PCT/US94/07314 filed June 27, 1994 (CIP of PCT/US 94/04278, filed 19 April 1994 ~~which in turn is a CIP of 957,290~~); ~~Serial No. 152,734, filed November 15, 1993; Serial No. 152,735, filed November 15, 1993; Serial No. 114,688, filed August 30, 1993.~~ The above patents and applications are specifically incorporated herein by reference.

FIELD OF THE INVENTION

The present invention is directed to novel gels and their uses.

BACKGROUND OF THE INVENTION

Air bags are intended to save lives, but the safety of air bags have been call into question after the deaths of several adults including children; and in one case, a child was decapitated by the force of an inflating air bag. The National Highway Traffic Safety Administration has issued warnings regarding the use of airbags in vehicles to protect occupants from impact and recommends that children and small adults not ride in the front passenger seat or that the front seat passenger air bag system be switched off or disengaged.

Conventional airbags are designed for rapid deployment by expanding pressurized or ignitable gas which advances the folded and tightly packed airbag almost instantaneously in the occupant's direction (Fig. 10a) with ~~violent~~ violent ~~fluxating~~ fluctuating force and with sufficient velocity to form a predetermined rigid or semi-rigid configuration when fully deployed. Although airbags are formed

of a flexible fabric, they are transformed into a substantially rigid or semi-rigid structure when rapidly inflated with gas providing resistance to collapse under impact conditions. In a crash, the air bag could hit with enough force (see Fig. 11 timing plot and Fig. 10a Bag pressure plot) to cause severe injuries or even death depending on the position of the passenger at the time of inflation.

Because ~~conventional~~ conventional airbags are made from woven fabric yarn material having great strength and resistance to fraying, the airbag construction require laser cutting, precision sewing, joining at the seams, and overlapping at the fabric ends. The define air bag volume also requires folding. The cost of a conventional airbag system is very high. Often time automobiles are stolen and the airbags removed to supply the after air bag market.

In general, reports and information on the state of the art conventional airbags, restraint systems, standards, tests methods, including glossary, ~~terminology~~ terminology and uses are found in the 1996 SAE Handbook, Vol. 3, pp 33.24-33.64 and Appendixes, On-Highway Vehicles and Off-Highway Machinery, Cooperative Engineering Program, and ASTM D 5426, 5645, and 5428.

Due to the severe punching force of conventional airbags (see Fig. ~~10A~~ 10a at 10, 20 and 30 msec profiles), what the world needs is a gentler, safer, more compact, and less expensive passenger friendly disposable airbags.

SUMMARY OF THE INVENTION

I have discovered more comfortable, soft, safe, hugging, ~~veloping~~ enveloping inflatable restraint cushions can be made ~~advantageously~~ advantageously from ~~predominantly~~ predominately liquid gels. Moreover, crystal gels made from thermoplastic elastomer copolymers and block copolymers having one or more substantially crystalline polyethylene segment midblocks exhibiting greater advantage over other non-crystalline component forming gels. The crystal gels ~~advantageously~~ advantageously exhibit high, higher, and ever higher tear resistances than ever realized before as well as improved high tensile strength. The crystal gels also exhibit improved damage tolerance, crack propagation resistance and especially improved resistance to high stress rupture which combination of properties makes the gels advantageously and surprisingly exceptionally more suitable for use as inflatable restraint cushions in vehicles such as in airplanes, high speed boats, trains, trucks, and automobiles than gels made from non-crystalline poly(ethylene) component copolymers.

The crystal gels which are advantageously useful for making ~~disposable~~ disposable inflatable restraint cushions comprises: 100 parts by weight of one or more high viscosity (I) linear triblock copolymers, (II) multi-arm block copolymers,

(III) branched block copolymers, (IV) radial block copolymers, (V) multiblock copolymers, (VI) random copolymers, (VII) thermoplastic crystalline polyurethane copolymers with hydrocarbon midblocks or mixtures of two or more (I)-(VII) copolymers in combination with or without major or minor amounts of one or more other (VIII) copolymers or polymers, said copolymers having one or more segments or one or more midblocks comprising one or more substantially crystalline polyethylene segments or midblocks and selected amounts of a ~~compatible~~ compatible plasticizer (IX) sufficient to achieve gel rigidities of from less than about 2 gram Bloom to about 1,800 gram Bloom with the proviso that when said (I)-(VII) copolymers having nil amorphous segment or nil amorphous midblock are combined with one or more (VIII) copolymers having one or more amorphous segments or amorphous midblocks to form a stable plasticizer ~~compatible~~ compatible gel.

As used herein, the term "gel rigidity" in gram Bloom is determined by the gram weight required to depress a gel a distance of 4 mm with a piston having a cross-sectional area of 1 square centimeter at ~~23°C~~ 23°C.

The gels comprising the thermoplastic elastomer copolymers and block copolymers having one or more substantially crystalline polyethylene segments or midblocks of the invention are hereafter referred to as "elastic-crystalline gels" or simpler "crystal gels". The segments or midblocks of copolymers forming the crystal gels of the invention are characterized by sufficient crystallinity as to exhibit a melting endotherm of at least about ~~40°C~~ 40°C as determined by DSC curve.

The various types of high viscosity copolymers and block copolymers employed in forming the crystal gels of the invention are of the general configurations ~~(Y-AY)_n~~ (Y-AY)_n copolymers, A-Z-A, and ~~(A-Z)_n~~ (A-Z)_n block copolymers, wherein the subscript n is two, three, four, five or more. In the case of multiarm block copolymers where n is 2, the block copolymer denoted by ~~(A-Z)_n~~ (A-Z)_n is A-Z-A. It is understood that the coupling agent is ignored for sake of simplicity in the description of the ~~(A-Z)_n~~ (A-Z)_n block copolymers.

The segment (A) comprises a glassy amorphous polymer end block segment which can be polystyrene, poly(alpha-methylstyrene), poly(o-methylstyrene), poly(m-methylstryene), poly(p-methylstyrene) and the like, preferably, polystyrene.

The segment (Y) of (VI) copolymers ~~(Y-AY)_n~~ (Y-AY)_n comprises substantially crystalline poly(ethylene) (simply denoted by "-E-" or (E)). In the case of (VI) copolymers ~~(A-Y)_n~~ (A-Y)_n, (Y) when next to (A) may be substantially non-crystalline or amorphous ethylene segments. For example a crystalline copolymer ~~(Y-AY)_n~~ (Y-AY)_n may be represented by:..... -E-E-E-E-E-E-E-E-E-SE-E-E-E-E-E-E-SE-E-E-E-E-E-E-SE-.... Where Y is a long run of polyethylenes or a non-crystalline copolymer ~~(AY-AY)_n~~ (AY-

AY_n: ...-E-SE-SE-E-SE-E-SE-E-SE-E-E-SE-SE-E-SE-...., Where Y is a non-crystalline run of ethylene.

The end block segment (A) comprises a glassy amorphous polymer end block segment which can be polystyrene, poly(alpha-methylstyrene), poly(o-methylstyrene), poly(m-methylstyrene), poly(p-methylstyrene) and the like, preferably, polystyrene. The segment (Y) of (VI) random copolymers A-Y comprises substantially crystalline poly(ethylene) (simply denoted by "-E-" or (E)). In the case of (VIII) random copolymers A-Y, (Y) may be substantially non-crystalline or amorphous ethylene segments. The midblocks (Z) comprises one or more midblocks of substantially crystalline poly(ethylene) (simply denoted by "-E- or (E)") with or without one or more amorphous midblocks of poly(butylene), poly(ethylene-butylene), poly(ethylene-propylene) or combination thereof (the amorphous midblocks are denoted by "-B- or (B)", "-EB- or (EB)", and "-EP- or (EP)" respectively or simply denoted by "-W- or (W)" when referring to one or more of the amorphous midblocks as a group) The A and Z, and A and Y portions are incompatible and form a two or more-phase system consisting of sub-micron amorphous glassy domains (A) interconnected by (Z) or (Y) chains. The glassy domains serve to crosslink and reinforce the structure. This physical elastomeric network structure is reversible, and heating the polymer above the softening point of the glassy domains temporarily disrupt the structure, which can be restored by lowering the temperature. During mixing and heating in the presence of ~~compatible~~ compatible plasticizers, the glassy domains (A) unlock due to both heating and solvation and the molecules are free to move when shear is applied. The disruption and ordering of the glassy domains can be viewed as a unlocking and locking of the elastomeric network structure. At equilibrium, the domain structure or morphology as a function of the (A) and (Z) or (A) and (Y) phases (mesophases) can take the form of spheres, cylinders, lamellae, or bicontinuous structures. The scale of separation of the phases are typically of the order of hundreds of angstroms, depending upon molecular weights (i.e. Radii of gyration) of the minority-component segments. At such small domain scales, when the gel is in the molten state while heated and brought into contact to be formed with any substrate and allowed to cool, the glassy domains of the gel become interlocked with the surface of the substrate. At sufficiently high enough temperatures, with or without the aid of other glassy resins, the glassy domains of the copolymers forming the gels fuses and interlocks with even a visibly smooth substrate surface such as glass. The disruption of the sub-micron domains due to heating above the softening point forces the glassy domains to open up, unlocking the network structure and flow. Upon cooling below the ~~softing~~ softening point, the glassy polymers reforms together into sub-micron domains, locking into a network structure once again,

resisting flow. It is this unlocking and locking of the network structure on the sub-micron scale with the surfaces of various materials which allows the gel to form interlocking composites with other materials. Such interlocking with many different materials produce gel composites having many uses.

The (I) linear block copolymers are characterized as having a Brookfield Viscosity value at 5 weight percent solids solution in toluene at ~~30°C~~ 30°C of from less than about 40 cps to about 60 cps and higher, advantageously from about 40 cps to about 160 cps and higher, more advantageously from about 50 cps to about 180 cps and higher, still more advantageously from about 70 cps to about 210 cps and higher, and even more advantageously from about 90 cps to about 380 cps and higher.

The (II, IV, and V) branched, star-shaped (radial), or multiarm block copolymers are characterized as having a Brookfield Viscosity value at 5 weight percent solids solution in toluene at ~~30°C~~ 30°C of from about 80 cps to about 380 cps and higher, advantageously from about 150 cps to about 260 cps and higher, more advantageously from about 200 cps to about 580 cps and higher, and still more advantageously from about 100 cps to about 800 cps and higher.

The crystal gels can be made in combination with a selected amount of one or more selected polymers and copolymers (II) including thermoplastic crystalline polyurethane elastomers with hydrocarbon blocks, homopolymers, copolymers, block copolymers, polyethylene copolymers, polypropylene copolymers, and the like described below.

The crystal gels of the invention are also suitable in physically interlocking or forming with other selected materials to form composites combinations. The materials are selected from the group consisting of paper, foam, plastic, fabric, metal, metal foil, concrete, wood, glass, various natural and synthetic fibers, including glass fibers, ceramics, synthetic resin, and refractory materials.

The high tear resistant soft crystal gels are ~~advantageously~~ advantageously suitable for a safer impact deployable air bag cushions, the higher tear resistant crystal gels are ~~advantageously~~ advantageously more suitable, and the highest tear resistant crystal gels are ~~advantageously~~ advantageously even more suitable for such use and other uses.

The various aspects and advantages will become apparent to those skilled in the art upon consideration of the accompanying disclosure.

The crystal gels of the invention can be formed into gel strands, gel tapes, gel sheets, and other articles of manufacture. ~~Moreover, because of their improved tear resistance and resistance to fatigue, the crystal gels exhibit versatility as balloons for medical uses, such as balloon for valvuloplasty of the mitral valve, gastrointestinal balloon dilator, esophageal balloon dilator, dilating balloon~~

~~catheter use in coronary angiogram and the like. Since the crystal gels are more tear resistant, they are especially useful for making condoms, toy balloons, and surgical and examination gloves. As toy balloons, the crystal gels are safer because it will not rupture or explode when punctured as would latex balloons which often times cause injuries or death to children by choking from pieces of latex rubber. The crystal gels are advantageously useful for making gloves, thin gloves for surgery and examination and thicker gloves for vibration damping which prevents damage to blood capillaries in the fingers and hand caused by handling strong shock and vibrating equipment.~~

The EB copolymer midblock of conventional SEBS is almost totally amorphous and the EP midblock of SEPS is amorphous and non-crystalline.

Gels made from such block copolymers are rubbery and exhibit substantially no hysteresis. Their rubbery-ness and lack of hysteresis are due to the amorphous nature of their midblocks.

Such gels are hereafter referred to as "non-crystalline gels" or more simply as "amorphous gels".

In general, the overall physical properties of amorphous gels are better at higher gel rigidities. The amorphous gels, however, can fail catastrophically when cut or notched while under applied forces of high dynamic and static deformations, such as extreme compression, torsion, high tension, high elongation, and the like. Additionally, the development of cracks or crazes resulting from a large number of deformation cycles can induce catastrophic fatigue failure of amorphous gel composites, such as tears and rips between the surfaces of the amorphous gel and substrates or at the interfaces of interlocking material(s) and gel. Consequently, such amorphous gels are inadequate for the most demanding applications involving endurance at high stress and strain levels over an extended period of time.

DESCRIPTION OF THE DRAWINGS

Figs. 1a-3m. Representative front views of frames for gel ~~diapharm~~ diaphragm pure volume expansions.

Figs. 3n-5b and ~~6a-6n~~ 6a-6m Representative sectional view of inflatable restraint gel ~~diapharm~~ diaphragm assemblies.

Figs. 5c-5m. Representative sectional view of various gel ~~diapharms~~ diaphragms.

Figs. 5n-5t. Representative sectional view of various gel ~~diapharms~~ diaphragms with ~~periferial~~ peripheral retainer.

Figs. ~~5u-5w~~ 5v-5w, 6n-6p. Representative sectional view of gel ~~diapharms~~ diaphragms with ~~periferial~~ peripheral retainer and expansion control elements.

Figs. 7a-7d. Representation sectional view of expanded gel ~~diapharms~~ diaphragms.

Figs. 7e-7h. Representation views of pure gel volume expansions ~~showing~~ showing various restriction conformations.

Figs. 2a-2e. Representation front views of ~~flangue~~ flange assemblies of expansion frames.

Figs. 8a-8f. Representation sectional view of gel ~~diapharms~~ diaphragms showing positions of various expansion films, sheets, and fabric.

Figs. 8g-8n. Representation front views of various films, sheets, thread and fabric patterns, ~~seorings~~ scoring, and ~~cutts~~ cuts.

Figs. 9a-9i. Representation of various gel ~~diapharm~~ diaphragm volume expansion configurations.

Fig. 10a. Conventional deployment timing profile of ~~passanger~~ passenger side bag in milliseconds.

Fig. 10b. Deployment timing profile of ~~passanger~~ passenger side volume expansion of gel ~~diapharm~~ in milliseconds.

Fig. 10c. Deployment timing profile of driver side volume expansion of gel ~~diapharm~~ diaphragm in milliseconds.

Fig. 10d. Deployment profile of driver side volume expansion of gel ~~diapharm~~ diaphragm showing enveloping cushion surround conformation on dummy.

Fig. 10e. Deployment profile of ~~passanger~~ passenger side volume expansion of gel ~~diapharm~~ diaphragm showing enveloping cushion surround conformation on dummy.

Fig. 11. Typical conventional air bag deployment pressure plot showing positive pressure A, cover break pressure point B, time from negative pressure to positive ~~presssure~~ pressure after cover tearseam break D, maximum air bag ~~preseure~~ pressure E.

Fig. 12. Typical invention gel ~~diapharm~~ diaphragm deployment pressure plot showing positive pressure A, cover break pressure point B, time to maximum positive ~~pressure~~ pressure after cover tearseam break E.

Figs. 13-15. Invention gel ~~diapharms~~ diaphragms ~~depolymnt~~ deployment pressure plots showing various selected maximum ~~pestitute~~ positive pressure absent tear covers.

Figs. 16, 17a, 17b, 17c, 17d, and 18-23. Illustrates composites of the invention.

DESCRIPTION OF THE INVENTION

Thermoplastic elastomer SEBS gels are described in my earlier applications and patents: U.S. Serial Nos: 581,188 filed 12/29/95; 581,191 filed 12/29/95; 581,125 filed 12/29/95; PCT/US94/04278 filed 4/19/94; PCT/US94/07314 filed 6/27/94; 288,690 filed 8/11/94; 152,734, filed 11/15/93; 152,735, 11/15/93; 114.688, filed 8/30/93; 935,540 filed 8/24/92; 876,118 filed 4/29/92; 705,096 filed 5/23/91; 527,058 filed 5/21/90; 921,752 filed 10/21/86; 458,703, filed 1/17/83; 916,731, filed 6/19/78; 815,315, filed 7/13/77; 778,343, filed 3/17/77; U.S. Patent Nos. 5,262,468; 5,153,254; 4,618,213; and 4,369,284. Various patents on thermoplastic elastomers and blends are described in U.S. Patent Nos. 3,595,942, Reissue 27,145-28,236; 3,772,234; 4,116,917; 4,687,815; and 4,880,878. Other non-patent publications related to S-EB-S polymers include: (1) W. P. Gergen, "Uniqueness of Hydrogenated Block Copolymers for Elastomeric Applications," presented at the German Rubber Meeting, Wiesbaden, 1983; Kautsch, Gummi, Kunstst. 37, 284 (1984). (2) W.P. Gergen, et al., "Hydrogenated Block Copolymers," Paper No. 57, presented at a meeting of the Rubber Division ACS, Los Angeles, April 25, 1985. Encyclopedia of Polymer Science and Engineering, Vol. 2, pp 324-434, "Block Copolymers". (3) L. Zotteri and et al., "Effect of hydrogenation on the elastic properties of poly(styrene-b-diene-b-styrene) copolymers", Polymer, 1978, Vol. 19, April. (4) J. Kenneth Craver, et al., Applied Polymer Science, Ch. 29, "Chemistry and Technology of Block Polymers", pp. 394-429, 1975. (5) Y. Mahajer and et al., "The influence of Molecular Geometry on the Mechanical Properties of homopolymers and Block Polymers of Hydrogenated Butadiene and Isoprene" reported under U.S. ARO Grant No. DAAG29-78-G-0201. (6) J. E. McGrath, et al., "Linear and Star Branched Butadiene-Isoprene Block Copolymers and Their Hydrogenated Derivatives", Chem. Dept, Virginia Polytechnic Institute and State University Blacksburg, VA, reported work supported by Army Research Office. (7) Legge, Norman R., "Thermoplastic Elastomers", Charles Goodyear Medal address given at the 131st Meeting of the Rubber Division, American Chemical Society, Montreal, Quebec, Canada, Vol. 60, G79-G115, May 26-29, 1987. (8) Falk, John Carl,

and et al., "Synthesis and Properties of Ethylene-Butylene-1 Block Copolymers", *Macromolecules*, Vol. 4, No. 2, pp. 152-154, March-April 1971. (9) Morton, Maurice, and et al., "Elastomeric Polydiene ABA Triblock Copolymers within Crystalline End Blocks", University of Arkon, work supported by Grant No. DMR78-09024 from the National Science Foundation and Shell Development Co. (10) Yee, A. F., and et al., "Modification of PS by S-EB-S Block Copolymers: Effect of Block Length", General Electric Corporate Research & Development, Schenectady, NY 12301. (11) Siegfried, D. L., and et al., "Thermoplastic Interpenetrating Polymer Networks of a Triblock Copolymer elastomer and an Ionomeric Plastic Mechanical Behavior", *Polymer Engineering and Science*, Jan. 1981, Vol. 21, No.1, pp 39-46. (12) Clair, D. J., "S-EB-S Copolymers Exhibit Improved Wax Compatibility", *Adhesives Age*, November, 1988. (13) Shell Chemical Technical Bulletin SC:1102-89, "Kraton® Thermoplastic Rubbers in oil gels", April 1989. (14) Chung P. Park and George P. Clingerman, "Compatibilization of Polyethylene-Polystyrene Blends with Ethylene-Styrene Random Copolymers", the Dow Chemical Company, May 1996. (15) Steve Hoenig, Bob Turley and Bill Van Volkenburgh, "Material Properties and Applications of Ethylene-Styrene Interpolymers", the Dow Chemical Company, September 1996. (16) Y. Wilson Cheung and Martin J. Guest, "Structure, Thermal Transitions and Mechanical Properties of Ethylene/Styrene Copolymers", the Dow Chemical Company, May 1996. (17) Teresa Plumley Karjaia, Y. Wilson Cheung and Martin J. Guest, "Melt Rheology and Processability of Ethylene/Styrene Interpolymers", the Dow Chemical Company, May 1997. The above applications, patents and publications are specifically incorporated herein by reference.

Legge's paper teaches the development of (conventional substantially amorphous elastomer midsegment) SEBS triblock copolymers. In the polymerization of butadiene by alkyl lithium initiators, 1,4-addition or 1,2-addition polymers, mixtures, can be obtained. In forming styrene butadiene triblock copolymers involving the addition of solvating agents such as ethers just before the final styrene charge is added, any excess of ethers can alter the polybutadiene structure from a 1,4-cis or trans structure to a 1,2- or 3,4-addition polymer. Using difunctional coupling agent would give linear block copolymers and multifunctional agents would give star-shaped or radial block copolymers. Hydrogenation of the 1,4-polybutadiene structure yields polyethylene, while that of the 1,2-polybutadiene yields polybutylene. The resulting polyethylene will be essentially identical with linear, high-density polyethylene with a melting point, T_m , of about ~~136°C~~ 136°C. Hydrogenation of 1,2-polybutadiene would yield atactic poly(1-butene) (polybutylene). The T_g of polybutylene is around ~~-18°C~~ -18°C. Random mixtures of ethylene and butylene units in the chain would suppress crystallinity arising from polyethylene sequences. The

objective for a good elastomer should be to obtain a saturated olefin elastomeric segment with the lowest possible T_g and the best elastomeric properties. Such an elastomer favored using styrene as the hard-block monomer and selecting the best monomer for hydrogenation of the elastomer midsegment. Using a mixture of 1,4- and 1,2-polybutadiene as the base polymer for the midsegment would result in an ethylene/butylene midsegment in the final product. The elements of selection of the midsegment composition is elastomer crystallinity and the elastomer T_g of an ethylene/butylene copolymer. Very low levels of crystallinity can be achieved around 40-50% butylene concentration. The minimum in dynamic hysteresis around 35% butylene concentration in the elastomeric copolymer. A value of 40% butylene concentration in the ethylene/butylene midsegment was chosen for the S-EB-S block copolymers.

Clair's paper teaches that the EB midblock of conventional S-EB-S polymers is a random copolymer of ethylene and 1-butene exhibiting nearly no crystallinity in the midblock. In the preparation of ethylene-butylene (EB) copolymers, the relative proportions of ethylene and butylene in the EB copolymer chain can be controlled over a broad range from almost all ethylene to almost all butylene. When the EB copolymer is nearly all ethylene, the methylene sequences will crystallize exhibiting properties similar to low density polyethylene. In differential scanning calorimeter (DSC) curves, the melting endotherm is seen on heating and a sharp crystallization exotherm is seen on cooling. As the amount of butylene in the EB copolymer is increased, the methylene sequences are interrupted by the ethyl side chains which shorten the methylene sequences length so as to reduce the amount of crystallinity in the EB copolymer. In conventional S-EB-S polymers, the amount of 1-butene is controlled at a high enough level to make the EB copolymer midblock almost totally amorphous so as to make the copolymer rubbery and soluble in hydrocarbon solvents. Clair suggests that an S-EB-S polymer retaining at least some crystallinity in the EB copolymer midblock may be desirable. Therefore, a new family of S-EB-S polymers are developed (U.S. Patent No. 3,772,234) in which the midblock contains a higher percentage of ethylene. The molecular weights of the new crystalline midblock segment S-EB-S polymers can vary from low molecular weight, intermediate molecular, to high molecular weight; these are designated Shell GR-3, GR-1, and GR-2 respectively. Unexpectedly, the highest molecular weight polymer, GR-2 exhibits an anomalously low softening point. A broad melting endotherm is seen in the DSC curves of these polymers. The maximum in this broad endotherm occurs at about ~~40°C~~ 40°C.

Himes, et al., (4,880,878) describes SEBS blends with improved resistance to oil absorption.

Papers (14) - (17) describes poly(ethylene-styrene) random copolymers (Dow

InterpolymersTM): Dow S, M and E Series produced by metallocene catalysts, using single site, constrained geometry addition polymerization catalysts resulting in poly(ethylene-styrene) random copolymers with weight average molecular weight (Mw) typically in the ~~range~~ range of ~~1 x 10⁵ to 4 x 10⁵~~ 1 x 10⁵ to 4 x 10⁵, and molecular weight ~~distributions~~ distributions (Mw/Mn) in the range of 2 to 3.

The type S series has more than 50 wt% styrene and is glassy at short times and rubbery at long times and exhibits ambient Tg. The type M series has more than 50 wt% styrene is amorphous rubber and exhibits very low modulus, high elasticity, low Tg. The type E series contains up to 50 wt% styrene is semi-crystalline rubber and exhibits low Tg, low modulus semi-crystalline, good compression set.

The E series random copolymers can be blended with the type M series copolymers and one or more of the I, II, III, IV, V, and VII copolymers to form crystalline polymer gel blends useful for the inflatable restraint cushions of the invention.

Block copolymers with polyethylene midblocks alone do not form suitable gels for purpose of the invention. Crystalline midblock regions needs to be balanced with amorphous midblock regions in order to obtain soft, flexible and elastic gels with the desired crystalline properties that are not found in totally amorphous gels.

The various representative crystalline/glassy domain/amorphous structures of S-E-EB-S, ~~S-EB45-EP-S~~ S-EB₄₅-EP-S, ~~S-E-EB25-S~~ S-E-EB₂₅-S, S-E-EP-E-S, S-EP-E-S and S-EP-E-EP-S are ~~illustrate in Figures 5-10 above~~ spheroids. Although the structure are spheroid representation, cylinders and plates are also within the scope of the present invention. Cylinder and plate structure are obtained with increasing glassy A end blocks. From about 15-30% by weight of A blocks, the block copolymer structure is spheroid. From about 33 about 40% by weight of A blocks, the block copolymer structure becomes cylindrical; and above about 45% A blocks, the structure becomes less cylindrical and more plate like.

In order to obtain elastic crystal gels of the invention, it is necessary that the selective synthesis of butadiene produce sufficient amounts of 1,4 poly(butadiene) that on hydrogenation can exhibit "crystallinity" in the midblocks. In order for the block copolymers forming the crystal gels of the invention to exhibit crystallinity, the crystalline midblock segments must contain long runs of -CH₂- groups. There should be approximately at least 16 units of ~~-(CH₂)-~~ CH₂ in sequence for crystallinity. Only the ~~-(CH₂)-~~₄ (CH₂)₄ units can crystallize, and then only if there are at least 4 units of ~~-(CH₂)-~~₄ (CH₂)₄ in sequence; alternatively, the polyethylene units are denoted by ~~-(CH₂-CH₂-CH₂-CH₂)-~~₄ [(CH₂-CH₂-CH₂-CH₂)]₄, ~~-(CH₂)-~~₄₄ [(CH₂)₄]₄ or ~~-(CH₂)-~~₁₆ (CH₂)₁₆, The amount of ~~-(CH₂)-~~₁₆ (CH₂)₁₆ units

forming the (E) midblocks of the block copolymers comprising the crystal gels of the invention should be at least about 20% which amount is capable of exhibiting a melting endotherm in differential scanning calorimeter ~~(DSC)~~ (DSC) curves.

Advantageously, the elastomer midblock segment should have a crystallinity of at least about 20% of ~~(-CH₂-)₁₆~~ (CH₂)₁₆ units of the total mole % forming the midblocks of the block copolymer, more advantageously at least about 25%, still more advantageously at least about 30%, especially advantageously at least about 40% and especially more advantageously at least about 50% and higher. Broadly, the crystallinity of the midblocks should range from at least about 20% to about 60%, less broadly from at least about 18% to about 65%, and still less broadly from at least 22% to about 70%.

The melting endotherm in DSC curves of the crystalline block copolymers comprising at least 20% crystallinity are much higher than conventional amorphous block copolymers. The maximum in the endotherm curves of the crystalline block copolymers occurs at about ~~40°C~~ 40°C, but can range from greater than about ~~25°C~~ 25°C to about ~~60°C~~ 60°C and higher. The crystalline block copolymers forming the crystal gels of the invention can exhibit melting endotherms (as shown by DSC) of about ~~25°C~~ 25°C to about ~~75°C~~ 75°C and higher. More specific melting endotherm values of the crystalline midblock block copolymers include: about ~~28°C, 29°C, 30°C, 31°C, 32°C, 33°C, 34°C, 35°C, 36°C, 37°C, 38°C, 39°C, 40°C, 41°C, 42°C, 43°C, 44°C, 45°C, 46°C, 47°C, 48°C, 49°C, 50°C, 51°C, 52°C, 53°C, 54°C, 55°C, 56°C, 57°C, 58°C, 59°C, 60°C, 61°C, 62°C, 63°C, 64°C, 65°C, 66°C, 67°C, 68°C, 69°C, 70°C, 71°C, 72°C, 73°C, 74°C, 75°C, 76°C, 77°C, 78°C, 79°C, 80°C, 90°C, 100°C, 110°C, 120°C~~ 28°C, 29°C, 30°C, 31°C, 32°C, 33°C, 34°C, 35°C, 36°C, 37°C, 38°C, 39°C, 40°C, 41°C, 42°C, 43°C, 44°C, 45°C, 46°C, 47°C, 48°C, 49°C, 50°C, 51°C, 52°C, 53°C, 54°C, 55°C, 56°C, 57°C, 58°C, 59°C, 60°C, 61°C, 62°C, 63°C, 64°C, 65°C, 66°C, 67°C, 68°C, 69°C, 70°C, 71°C, 72°C, 73°C, 74°C, 75°C, 76°C, 77°C, 78°C, 79°C, 80°C, 90°C, 100°C, 110°C, 120°C, and higher, whereas, the melting endotherm (DSC) for conventional amorphous midblock segment block copolymers are about ~~10°C~~ 10°C and lower.

The melting endotherm is seen on heating and a sharp crystallization exotherm is seen on cooling. Such midblock crystallization endothermic and exothermic characteristics are missing from ~~DSC~~ DSC curves of amorphous gels. The crystallization exotherm and fusion endotherm of the crystalline block copolymer gels of the invention are determined by ASTM D 3417 method.

Generally, the method of obtaining long runs of crystalline ~~(-CH₂-)~~ CH₂ is by sequential block copolymer synthesis followed by hydrogenation. The attainment of crystal gels of the instant invention is solely due to the selective polymerization of the butadiene monomer (forming the midblocks) resulting in one or more

predetermined amount of 1,4 poly(~~butadiene~~ butadiene) blocks followed by sequential polymerization of additional midblocks and hydrogenation to produce one or more crystalline midblocks of the final block copolymers.

The crystalline block copolymers are made by sequential block copolymer synthesis, the percentage of crystallinity or $\text{-(CH}_2\text{)-}_{16} \text{(CH}_2\text{)}_{16}$ units should be at least about $\text{-(0.67)-}_4 \text{(0.67)}_4$ or about 20% and actual crystallinity of about 12%. For example, a selectively synthesized S-EBn-S copolymer having a ratio of 33:67 of 1,2 and 1,4 poly(butadiene) on hydrogenation will result in a midblock with a crystallinity of $\text{-(0.67)-}_4 \text{(0.67)}_4$ or 20%. For sake of simplicity, when n is a subscript of -EB-, n denotes the percentage of $\text{-(CH}_2\text{)-}_4 \text{(CH}_2\text{)}_4$ units, eg, n = 33 or 20% crystallinity which is the percentage of (0.67)₄ or " $\text{-(CH}_2\text{)-}_{16} \text{(CH}_2\text{)}_{16}$ " units. Thus, when n = 28 or 72% of $\text{-(CH}_2\text{)-}_4 \text{(CH}_2\text{)}_4$ units, the % crystallinity is $\text{-(0.72)-}_4 \text{(0.72)}_4$ or 26.87% crystallinity attributed to $\text{-(CH}_2\text{)-}_{16} \text{(CH}_2\text{)}_{16}$ units, denoted by -~~EB28-~~ EB₂₈. As a matter of convention, and for purposes of this specification involving hydrogenated polybutadiene: the notation -E- denotes at least about 85% of $\text{-(CH}_2\text{)-}_4 \text{(CH}_2\text{)}_4$ units. The notation -B- denotes at least about 70% of $\text{-(CH}_2\text{-CH(C}_2\text{H}_5\text{))-}_1 \text{[-CH}_2\text{-CH(C}_2\text{H}_5\text{)-]}_1$ units. The notation -EB- denotes between about 15 and 70% $\text{-(CH}_2\text{-CH(C}_2\text{H}_5\text{))-}_1 \text{[-CH}_2\text{-CH(C}_2\text{H}_5\text{)-]}_1$ units. The notation -EBn- denotes n% $\text{-(CH}_2\text{-CH(C}_2\text{H}_5\text{))-}_1 \text{[-CH}_2\text{-CH(C}_2\text{H}_5\text{)-]}_1$ units. For hydrogenated polyisoprene: The notation -EP- denotes about at least 90% $\text{-(CH}_2\text{-CH(CH}_3\text{))-CH}_2\text{-CH}_2\text{-}_1 \text{[-CH}_2\text{-CH(CH}_3\text{)-CH}_2\text{-CH}_2\text{-]}_1$ units.

Generally, one or more (E) midblocks can be incorporated at various positions along the midblocks of the block copolymers. Using the sequential process for block copolymer synthesis, The (E) midblocks can be positioned as follows:

- i) A-E-W-A
- ii) A-E-W-E-A
- ii) A-W-E-W-A
- iii) A-E-W-E-W-E-W-E-A
- iv) A-W-E-W-A-E-A-E-W-E-A
- v) and etc.

The lower flexibility of block copolymer crystal gels due to (E) midblocks can be balanced by the addition of sequentially (W) midblocks. For example, the sequentially synthesized block copolymer S-E-EB-S can maintain a high degree of flexibility due to the presence of amorphous -EB- block. The sequential block copolymer S-E-EB-B-S can maintain a high degree of flexibility due to the presence

of amorphous -EB- and -B- midblocks. The sequential block copolymer S-E-EP-E-S can maintain a high degree of flexibility due to the presence of -EP- midblock. The sequential block copolymer S-E-B-S can maintain a high degree of flexibility due to the presence of the -B- midblock. For S-E-S, where the midblock is substantially crystalline and flexibility low, physical blending with amorphous block copolymers such as S-EB-S, S-B-S, S-EP-S, S-E-EP-S, S-EB-EP-S, ~~(S-EP)_n~~ (S-EP)_n and the like can produce more softer, less rigid, and more flexible crystal gel.

Because of the (E) midblocks, the crystal gels of the invention exhibit different physical characteristics and improvements over substantially amorphous gels including damage tolerance, improved crack propagation resistance, improved tear resistance producing knotty tears as opposed to smooth tears, crystalline melting point of at least ~~20°C~~ 28°C, improved resistance to fatigue, higher hysteresis, etc. Moreover, the crystal gels when stretched exhibit additional yielding as shown by necking caused by stress induced crystallinity. Additionally, the crystallization rates of the crystalline midblocks can be controlled and slowed depending on thermal history producing time delay recovery upon deformation.

Regarding resistance to fatigue, fatigue (as used herein) is the decay of mechanical properties after repeated application of stress and strain. Fatigue tests give information about the ability of a material to resist the development of cracks or crazes resulting from a large number of deformation cycles. Fatigue test can be conducted by subjecting samples of amorphous and crystal gels to deformation cycles to failure (appearance of cracks, crazes, rips or tears in the gels).

Tensile strength can be determined by extending a selected gel sample to break as measured at ~~100°~~ 180° U bend around a 5.0 mm mandrel attached to a spring scale. Likewise, tear strength of a notched sample can be determined by propagating a tear as measured at ~~100°~~ 180° U bend around a 5.0 mm diameter mandrel attached to a spring scale.

Various block copolymers can be obtained which are amorphous, highly rubbery, and exhibiting minimum dynamic hysteresis:

Block copolymer S-EB-S

The monomer butadiene can be polymerized in a ether/hydrocarbon solvent to give a 50/50 ratio of 1,2 poly(butadiene)/1,4 poly(butadiene) and on hydrogenation no long runs of ~~-CH₂-~~ CH₂ groups and negligible crystallinity, ie, about ~~(0.5)₄~~ (0.5)₄ or 0.06 or 6% and actual crystallinity of about 3%. Due to the constraints of Tg and minimum hysteresis, conventional S-EB-S have ethylene-butylene ratios of about 60:40 with a crystallinity of about ~~(0.6)₄~~ (0.6)₄ or 0.129 or 12% and actual crystallinity of about 7.7%.

Block copolymer S-EP-S

The monomer isoprene when polymerized will produce 95% 1,4 poly(isoprene)/5% 3,4 poly(isoprene) and upon hydrogenation will form amorphous, rubbery poly(ethylene-propylene) midblock and no long runs of $-\text{CH}_2-\text{CH}_2-$ and no crystallinity.

Mixed block copolymer S-EB/EP-S

The polymerization of a 50/50 mixture of isoprene/butadiene monomers in suitable ether/hydrocarbon solvents to give equal amounts of 1,2 and 1,4 poly(butadiene) on hydrogenation will produce a maximum crystallinity of ~~(0.25)~~⁴ (0.25)⁴ or 0.4%. The actual crystallinity would be approximately about 0.2%, which is negligible and results in a good rubbery midblock.

The polymerization of a 80/20 mixture of isoprene/butadiene monomers in suitable ether/hydrocarbon solvents to give equal amounts of 1,2 and 1,4 poly(butadiene) will upon hydrogenation produce a low crystallinity of ~~(0.10)~~⁴ (0.10)⁴ or 0.01%. The actual crystallinity would be approximately about 0.006%, which is negligible and results in a good rubbery midblock.

The polymerization of a 20/80 mixture of isoprene/butadiene monomers in suitable ether/hydrocarbon solvents to give equal amounts of 1,2 and 1,4 poly(butadiene) will upon hydrogenation produce a low crystallinity of ~~(0.4)~~⁴ (0.4)⁴ or 2.56%. The actual crystallinity would be approximately about 1.53%, which is negligible and results in a good rubbery midblock.

The polymerization of a 20/80 mixture of isoprene/butadiene monomers in suitable ether/hydrocarbon solvents to give a 40:60 ratio of 1,2 and 1,4 poly(butadiene) will upon hydrogenation produce a low crystallinity of ~~(0.48)~~⁴ (0.48)⁴ or 5.3%. The actual crystallinity would be approximately about 3.2%, which is negligible and results in a good rubbery midblock.

For purpose of convince and simplicity, the hydrogenated polybutadiene are denoted as follows: -E- denotes at least 85% R-1 units, -B- denotes at least 70% R-2 units, -EB- denotes between 15 and 70% R-2 units, ~~-EB_n~~ -EB_n denotes n% R-2 units, and -EP- denotes 90% R-3 units.

$$\begin{array}{c}
 |H_2 \\
 \text{---(CH}_2\text{)}_4\text{---(CH-CH}_2\text{)---(CH}_2\text{-CH-CH}_2\text{-CH}_2\text{)-(CH}_2\text{-CH)-} \\
 C_2H_5 \qquad CH_3 \qquad CH \\
 CH_3 \quad CH_3 \\
 |H_2 \\
 \text{---(CH}_2\text{)}_4\text{---(CH-CH}_2\text{)---(CH}_2\text{-CH-CH}_2\text{-CH}_2\text{)-(CH}_2\text{-CH)-} \\
 C_2H_5 \qquad CH_3 \qquad CH \\
 CH_3 \quad CH_3
 \end{array}$$

(1-n)% from polyisoprene

$$5\% \cdot (1-n)$$

n =	R-1	R-2	R-3	R-4
0%	0%	0%	95%	5%
20%	18%	2%	76%	4%
40%	36%	4%	57%	3%
60%	54%	6%	38%	2%
80%	72%	8%	19%	1%
100%	90%	10%	0%	0%

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R-2 denotes $\text{---}(\text{CH}-\text{CH}_2)\text{---}$,
 $\text{---C}_2\text{H}_5$



R-3 denotes $\text{---}(\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}_2)\text{---}$ $(\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}_2)$ and,
 $\text{---CH}_3\text{---}$ CH_3

R-4 denotes $\text{---}(\text{CH}_2-\text{CH})\text{---}$ (CH_2-CH)
 $\text{CH}\text{---}$ CH
 $\text{---CH}_3-\text{CH}_3\text{---}$ CH_3-CH_3

Therefore, the percentage that can crystallize is $\text{---}(\text{CH}_2-\text{CH}_2)\text{---}$ $[(\text{CH}_2-\text{CH}_2)_4]_4$ since this is the chance of getting four $\text{---}(\text{CH}_2-\text{CH}_2)\text{---}$ $(\text{CH}_2-\text{CH}_2)_4$ units in sequence. The percentage that will crystallize is about 60% of this.

n =	$(\text{CH}_2-\text{CH}_2)_4$	$[(\text{CH}_2-\text{CH}_2)_4]_4$	$0.6 \times [(\text{CH}_2-\text{CH}_2)_4]_n$
n =	$\text{---}(\text{CH}_2-\text{CH}_2)\text{---}$	$\text{---}(\text{CH}_2-\text{CH}_2)\text{---}$	$0.6 \times \text{---}(\text{CH}_2-\text{CH}_2)\text{---}$
0%	0%	0%	0%
20%	18%	0.1%	0.06%
40%	36%	1.7%	1.0%
60%	54%	8.5%	5.1%
80%	72%	26.9%	16.1%
100%	90%	65.6%	39.4%

This applies to polymerization in a hydrocarbon solvent. In an ether (eg, diethylether), the percentage $\text{---}(\text{CH}_2-\text{CH}_2)\text{---}$ $(\text{CH}_2-\text{CH}_2)_4$ units will be reduced so that crystallinity will be negligible negligible.

n =	$(-\text{CH}_2-)_4$	$[(-\text{CH}_2-)_4]_4$	$0.6 \times [(-\text{CH}_2-)_4]_n$
n =	$(-\text{CH}_2-)_4$	$[(-\text{CH}_2-)_4]_4$	$0.6 \times [(-\text{CH}_2-)_4]_n$
0%	0%	0%	0%
20%	5%	0.0006%	0.0004%
40%	10%	0.01%	0.006%
60%	15%	0.05%	0.03%
80%	20%	0.16%	0.10%
100%	25%	0.39%	0.23%

These values are all negligible. There will be no detectable crystallinity in any of these polymer midblocks. In a mixed ether/hydrocarbon solvent, values will be intermediate, depending on the ratio of ether to hydrocarbon.

The midblocks (Z) of one or more -E-, -B-, -EB-, or -EP- can comprise various combinations of midblocks between the selected end blocks (A); these include: -E-EB-, -E-EP-, -B-EP-, -B-EB-, -E-EP-E-, -E-EB-B-, -B-EP-B-, -B-EB-B-, -E-B-EB-, -E-B-EP-, -EB-EP-, -E-EB-EP-, -E-EP-EB-, -B-EB-EP-, -B-EP-EB-, -E-EP-E-EP-, -E-EP-E-EB-, -B-EP-B-EP-, -B-EB-B-EB-, -B-EB-B-EP-, -E-EB-B-EP-, -E-EP-B-EB-, -E-EP-E-EP-E-, -B-EP-B-EP-B-, -E-EP-E-EB-, -E-EP-E-EP-EB-, -E-EP-E-EP-E-, -E-EP-EB-EP-EB-B- and the like.

The block copolymers of (A-Z-A) can be obtained by sequential synthesis methods followed by hydrogenation of the midblocks. As denoted above, abbreviations are interchangeably used, for example, (S-E-EP-S) denotes poly(styrene-ethylene-ethylene-co-propylene-styrene). Other linear block copolymers (denoted in abbreviations) include the following:

(S-E-EB-S), (S-E-EP-S), (S-B-EP-S), (S-B-EB-S), (S-E-EP-E-S), (S-E-EB-B-S), (S-B-EP-B-S), (S-B-EB-B-S), (S-E-B-EB-S), (S-E-B-EP-S), (S-EB-EP-S), (S-E-EB-EP-S), (S-E-EP-EB-S), (S-B-EB-EP-S), (S-B-EP-EB-S), (S-E-EP-E-EP-S), (S-E-EP-E-EB-S), (S-EP-B-EP-S), (S-B-EB-B-EB-S), (S-B-EB-B-EP-S), (S-E-EB-B-EP-S), (S-E-EP-B-EB-S), (S-E-EP-E-EP-E-S), (S-B-EP-B-EP-B-S), (S-E-EP-E-EB-S), (S-E-EP-E-EP-EB-S), (S-E-EP-E-EP-E-S), (S-E-EP-EB-EP-EB-B-S), (S-E-EP-EB-EP-EB..... -S) and the like.

The multiblock star-shaped (or radial) copolymers $(A-Z)_n \times (A-Z)_n$ can be obtained by sequential synthesis methods including hydrogenation of selected block

copolymers made by polymerizing half of the block copolymers such as SBS or SIS and couple the halves with a coupling agent such as an organic dihalide; or couple with an agent such as ~~SnCl₄~~ SnCl₄, which ~~results~~ results in star-shaped block copolymers (four branches). Coupling with divinyl benzene give block copolymers which are very highly branched. Radial block copolymers suitable for use in forming the crystal gels of the present invention include: ~~(S-E-EB-S)_n, (S-E-EP)_n, (S-B-EP)_n, (S-B-EB)_n, (S-E-EP-E)_n, (S-E-EB-B)_n, (S-B-EP-B)_n, (S-B-EB-B)_n, (S-E-B-EB)_n, (S-E-B-EP)_n, (S-EB-EP)_n, (S-E-EB-EP)_n, (S-E-EP-EB)_n, (S-B-EB-EP)_n, (S-B-EP-EB)_n, (S-E-EP-E-EP)_n, (S-E-EP-E-EB)_n, (S-EP-B-EP)_n, (S-B-EB-B-EB)_n, (S-B-EB-B-EP)_n, (S-E-EB-B-EP)_n, (S-E-EP-B-EB)_n, (S-E-EP-E-EP-E)_n, (S-B-EP-B-EP-B)_n, (S-E-EP-E-EB)_n, (S-E-EP-E-EP-EB)_n, (S-E-EP-E-EP-E)_n, (S-E-EP-EB-EP-EB-B)_n~~ (S-E-EB-S)_n, (S-E-EP)_n, (S-B-EP)_n, (S-B-EB)_n, (S-E-EP-E)_n, (S-E-EB-B)_n, (S-B-EP-B)_n, (S-B-EB-B)_n, (S-E-B-EB)_n, (S-E-B-EP)_n, (S-EB-EP)_n, (S-E-EB-EP)_n, (S-E-EP-EB)_n, (S-B-EB-EP)_n, (S-B-EP-EB)_n, (S-E-EP-E-EP)_n, (S-E-EP-E-EB)_n, (S-EP-B-EP)_n, (S-B-EB-B-EB)_n, (S-B-EB-B-EP)_n, (S-E-EB-B-EP)_n, (S-E-EP-B-EB)_n, (S-E-EP-E-EP-E)_n, (S-B-EP-B-EP-B)_n, (S-E-EP-E-EB)_n, (S-E-EP-E-EP-EB)_n, (S-E-EP-E-EP-E)_n, (S-E-EP-EB-EP-EB-B)_n.

The selected amount of crystallinity in the midblock should be sufficient to achieve improvements in one or more physical properties including improved damage tolerance, improved crack propagation resistance, improved tear resistance, improved resistance to fatigue of the bulk gel and resistance to catastrophic fatigue failure of crystal gel composites, such as between the surfaces of the crystal gel and substrate or at the interfaces of the interlocking material(s) and crystal gel, which improvements are not found in amorphous gels at corresponding gel rigidities.

As an example, when fabric interlocked or saturated with amorphous S-EB-S gels (gel composites) are used as gel liners for lower limb or above the knee prosthesis to reduce pain over pressure areas and give relief to the amputee, the commonly used amorphous gels forming the liners can tear or rip apart during marathon racewalk after 50-70 miles. In extended use, the amorphous gels can rip on the bottom of the liner in normal racewalk training of 40-60 miles over a six weeks period. In such demanding applications, the crystal gels are especially advantageous and is found to have greater tear resistance and resistance to fatigue resulting from a large number of deformation cycles than amorphous gels.

Selected (I) linear block and radial copolymers utilized in forming the crystal gels of the invention are characterized as having an ethylene to butylene midblock ratio (E:B) of about 85:15 to about 65:35. Advantageously, the butylene concentration of the midblock is about 35% or less, more advantageously, about 30% or less, still more advantageously, about 25% or less, especially advantageously,

about 20% or less. Advantageously, the ethylene to butylene midblock ratios can range from about 89:11, 88:12, 87:13, 86:14, 85:15, 84:16, 83:17, 82:18, 81:19, 80:20, 79:21, 78:22, 77:23, 76:24, 75:25, 74:26, 73:27, 72:28, 71:29, 70:30, 69:31, 68:32, 67:33, 66:34 to about 65:35.

The A to Z midblock ratio of the block copolymers suitable for forming crystal gels of the invention can range from about 20:80 to 40:60 and higher. More specifically, the values can be 15:85, 19:81, 20:80, 21:79, 22:78, 23:77, 24:76, 25:75, 26:74, 27:73, 28:72, 29:71, 30:70, 31:69, 32:68, 33:67, 34:66, 35:65, 36:64, 37:63, 38:62, 39:61, 40:60, 41:59, 42:58, 43:57, 44:65, 45:55, 46:54, 47:53, 48:52, 49:51, 50:50, 51:49 and 52:48.

The crystal gels can optionally comprise selected major or minor amounts of one or more polymers or copolymers (II) provided the amounts and combinations are selected without substantially decreasing the desired properties. The polymers and copolymers can be linear, star-shaped (radial), branched, or multiarm; these including: (SBS) styrene-butadiene-styrene block copolymers, (SIS) styrene-isoprene-styrene block copolymers, low and medium viscosity (S-EB-S) styrene-ethylene-butylene-styrene block copolymers, (S-EP) styrene-ethylene-propylene block copolymers, (S-EP-S) styrene-ethylene/propylene-styrene block copolymers, (S-E-EPS) styrene-ethylene-ethylene/propylene-styrene block copolymers, ~~(SB)_n~~ (SB)_n styrene-butadiene and ~~(S-EB)_n~~, ~~(S-EB-S)_n~~, ~~(S-E-EP)_n~~, ~~(SEP)_n~~ (S-EB)_n, (S-EB-S)_n, (S-E-EP)_n, (SEP)_n, (SI)_n, ~~(GI)_n~~ multi-arm, branched or star-shaped copolymers, polyethyleneoxide (EO), poly(dimethylphenylene oxide), teflon (TFE, PTFE, PEA, FEP, etc), optical clear amorphous copolymers based on 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole (PDD) and tetrafluoroethylene (TFE), maleated S-EB-S block copolymer, polycarbonate, ethylene vinyl alcohol copolymer, and the like. Still, other (II) polymers include homopolymers which can be utilized in minor amounts; these include: polystyrene, polydimethylsiloxane, polyolefins such as polybutylene, polyethylene, polyethylene copolymers, polypropylene, and the like. Polyurethane elastomers based on saturated hydrocarbon diols (Handlin, D., Chin. S., and Masse. M., et al. "POLYURETHANE ELASTOMERS BASED ON NEW SATURATED HYDROCARBON DIOLS" Published Society of Plastics Industry, Polyurethane Division, Las Vegas, October 23, 1996) are also suitable for use in blending with the block copolymers (I) used in forming the crystal gels of the invention. Such saturated hydrocarbon diols include hydroxyl terminated oligomers of poly(ethylene-butylene) (EB), poly(ethylene-propylene) (EP), -E-EB-, -E-EP-, -B-EP-, -B-EB-, -E-EP-E-, -E-EB-B-, -B-EP-B-, -B-EB-B-, -E-B-EB-, -E-B-EP-, -EB-EP-, -E-EB-EP-, -E-EP-EB-, -B-EB-EP-, -B-EP-EB-, -E-EP-E-EP-, -E-EP-E-EB-, -B-EP-B-EP-, -B-EB-B-EB-, -B-EB-B-EP-, -E-EB-B-EP-, -E-EP-B-EB-, -E-EP-E-EP-E-, -B-EP-B-EP-B-, -E-EP-E-EB-, -E-EP-E-EP-EB-, -E-EP-E-

EP-E-, -E-EP-EB-EP-EB-B- and the like. As an example, thermoplastic polyurethane made with isocyanates and chain extenders such as TMPD and BEPD from saturated hydrocarbon diol KLP L-2203 having a hard segment contents of 22% exhibits clean phase separation of the hard and soft segments with glass a transition of ~~-50°C~~ -50°C. KLP L-2203 based TPU's can be mixed with the crystalline block copolymers to form soft crystal gels within the gel rigidity ranges of the invention.

Suitable polyolefins include polyethylene and polyethylene copolymers such as Dow Chemical Company's Dowlex 3010, 2021D, 2038, 2042A, 2049, 2049A, 2071, 2077, 2244A, 2267A; Dow Affinity ethylene alpha-olefin resin PL-1840, SE-1400, SM-1300; more suitably: Dow Elite 5100, 5110, 5200, 5400, Primacor 141-XT, 1430, 1420, 1320, 3330, 3150, 2912, 3340, 3460; Dow Attane (ultra low density ethylene-octene-1 copolymers) 4803, 4801, 4602,

The conventional term "major" means about 51 weight percent and higher (e.g. 55%, 60%, 65%, 70%, 75%, 80% and the like) and the term "minor" means 49 weight percent and lower (e.g. 2%, 5%, 10%, 15%, 20%, 25% and the like).

Example of (II) polymers, copolymers, and blends include: (a) Kraton G 1651, G 1654X; (b) Kraton G 4600; (c) Kraton G 4609; other suitable high viscosity polymer and oils include: (d) Tuftec H 1051; (e) Tuftec H 1041; (f) Tuftec H 1052; (g) Kuraray SEPS 4033; (h) Kuraray S-EB-S 8006; (i) Kuraray SEPS 2005; (j) Kuraray SEPS 2006 , and (k) blends (polyblends) of (a)-(h) with other polymers and copolymers include: (1) S-EB-S/SBS; (2) S-EB-S/SIS; (3) S-EB-S/(SEP); (4) S-EB-S/(SEB)n; (5) S-EB-S/(SEB)n; (6) S-EB-S/(SEP)n; (7) S-EB-S/(SI)n; (8) S-EB-S/(SI) multiarm; (9) S-EB-S/(SEB)n; (10) (SEB)n star-shaped copolymer; (11) s made from blends of (a)-(k) with other homopolymers include: (12) S-EB-S/polystyrene; (13) S-EB-S/polybutylene; (14) S-EB-S/poly-ethylene; (14) S-EB-S/polypropylene; (16) SEP/S-EB-S, (17) SEP/SEPS, (18) SEP/SEPS/SEB, (19), SEPS/S-EB-S/SEP, (20), SEB/S-EB-S (21), EB-EP/S-EB-S (22), S-EB-S/EB (23), S-EB-S/EP (24), (25) (SEB)n s, (26) (SEP)n, (27) Kuraray 2007 (SEPS), (28) Kuraray 2002, (SEPS), (29) Kuraray 4055 (S-EB-EP-S) (30) Kuraray 4077 (S-EB-EP-S) (31) Kuraray 4045 (S-EB-EP-S) (32) (S-EB-EP)n, (33) (SEB)n, (34) EPDM, (35) EPR, (36) EVA, (37) coPP, (38) EMA, (39) EEA, (40) DuPont Teflon AF amorphous fluoropolymers, (41) Dow polydimethylsiloxane, (42) maleated S-EB-S (maleation level 2-30%), (43) (EP)n and the like.

Representative examples of commercial elastomers that can be combined with the block copolymers (I) described above include: Shell Kratons D1101, D1102, D1107, D1111, D1112, D1113X, D1114X, D1116, D1117, D1118X, D1122X, D1125X, D1133X, D1135X, D1184, D1188X, D1300X, D1320X, D4122, D4141, D4158, D4240, G1650, G1652, G1657, G1701X, G1702X, G1726X, G1750X, G1765X, FG1901X, FG1921X, D2103, D2109, D2122X, D3202, D3204, D3226, D5298, D5999X, D7340, G1650, G1651, G1652, G4609, G4600,

G1654X, G2701, G2703, G2705, G1706, G2721X, G7155, G7430, G7450, G7523X, G7528X, G7680, G7705, G7702X, G7720, G7722X, G7820, G7821X, G7827, G7890X, G7940, FG1901X and FG1921X. Kuraray's SEP, SEPS, S-EB-S, S-EB-EP-S Nos. 1001, 1050, 2027, 2003, 2006, 2007, 2008, 2023, 2043, 2063, 2050, 2103, 2104, 2105, 4033 (SEEPS), 4045 (SEEPS), 4055 (SEEPS), 4077 (SEEPS), 8004, 8006, 8007, H-VS-3 (S-V-EP)N, and the like.

The amorphous S-EB-S and (S-EB)_n (II) copolymers can have a broad range of styrene to ethylene-butylene ratios (S:EB) of about 20:80 or less to about 40:60 or higher. The S:EB weight ratios can range from lower than about 20:80 to above about 40:60 and higher. More specifically, the values can be 15:85, 19:81, 20:80, 21:79, 22:78, 23:77, 24:76, 25:75, 26:74, 27:73, 28:72, 29:71, 30:70, 31:69, 32:68, 33:67, 34:66, 35:65, 36:64, 37:63, 38:62, 39:61, 40:60, 41:59, 42:58, 43:57, 44:65, 45:55, 46:54, 47:53, 48:52, 49:51, 50:50, 51:49, 52:48 and etc. Other ratio values of less than 19:81 or higher than 51:49 are also possible. Broadly, the styrene block to elastomeric block ratio of the high viscosity liner and star copolymers is about 20:80 to about 40:60 or higher, less broadly about 31:69 to about 40:60, preferably about 32:68 to about 38:62, more preferably about 32:68 to about 36:64, particularly more preferably about 32:68 to about 34:66, especially more preferably about 33:67 to about 36:64, and still more preferably about 30:70.

The Brookfield Viscosity of a 5 weight percent solids solution in toluene at ~~30°C~~ 30°C of 2006, 4045 (SEEPS), 4055 (SEEPS), 4077 (SEEPS) typically range about 20-35, about 25-150, about 60-150, about 200-400 respectively. Typical Brookfield Viscosities of a 10 weight percent solids solution in toluene at ~~30°C~~ 30°C of 1001, 1050, 2007, 2063, 2043, 4033, 2005, 2006, are about 70, 70, 17, 29, 32, 50, 1200, and 1220 respectively. Typical Brookfield Viscosity of a 25 weight percent solids solution in toluene at ~~25°C~~ 25°C of Kraton D1101, D1116, D1184, D1300X, G1701X, G1702X are about 4000, 9000, 20000, 6000, 50000 and 50000 cps respectively. Typical Brookfield Viscosity of a 10 weight percent solids solution in toluene at ~~25°C~~ 25°C of G1654X is about 370 cps. The Brookfield Viscosities of a 20 and 30 weight percent solids solution in toluene at ~~30°C~~ 30°C of H-VS-3 are about 133 cps and 350 cps respectively.

Suitable block copolymers (II) and their typical viscosities are further described. Shell Technical Bulletin SC:1393-92 gives solution viscosity as measured with a Brookfield model RVT viscometer at ~~25°C~~ 25°C for Kraton G 1654X at 10% weight in toluene of approximately 400 cps and at 15% weight in toluene of approximately 5,600 cps. Shell publication SC:68-79 gives solution viscosity at ~~25°C~~ 25°C for Kraton G 1651 at 20 weight percent in toluene of approximately 2,000 cps. When measured at 5 weight percent solution in toluene at ~~30°C~~ 30°C, the solution

viscosity of Kraton G 1651 is about 40. Examples of high viscosity S-EB-S triblock copolymers includes Kuraray's S-EB-S 8006 which exhibits a solution viscosity at 5 weight percent at ~~30°C~~ 30°C of about 51 cps. Kuraray's 2006 SEPS polymer exhibits a viscosity at 20 weight percent solution in toluene at ~~30°C~~ 30°C of about 78,000 cps, at 5 weight percent of about 27 cps, at 10 weight percent of about 1220 cps, and at 20 weight percent 78,000 cps. Kuraray SEPS 2005 polymer exhibits a viscosity at 5 weight percent solution in toluene at ~~30°C~~ 30°C of about 28 cps, at 10 weight percent of about 1200 cps, and at 20 weight percent 76,000 cps. Other grades of S-EB-S, SEPS, (SEB)_n, (SEP)_n polymers can also be utilized in the present invention provided such polymers exhibits the required high viscosity. Such S-EB-S polymers include (high viscosity) Kraton G 1855X which has a Specific Gravity of 0.92, Brookfield Viscosity of a 25 weight percent solids solution in toluene at ~~-25°C~~ 25°C of about 40,000 cps or about 8,000 to about 20,000 cps at a 20 weight percent solids solution in toluene at ~~-25°C~~ 25°C.

The styrene to ethylene and butylene (S:EB) weight ratios for the Shell designated polymers can have a low range of 20:80 or less. Although the typical ratio values for Kraton G 1651, 4600, and 4609 are approximately about 33:67 and for Kraton G 1855X approximately about 27:73, Kraton G 1654X (a lower molecular weight version of Kraton G 1651 with somewhat lower physical properties such as lower solution and melt viscosity) is approximately about 31:69, these ratios can vary broadly from the typical product specification values. In the case of Kuraray's S-EB-S polymer 8006 the S:EB weight ratio is about 35:65. In the case of Kuraray's 2005 (SEPS), and 2006 (SEPS), the S:EP weight ratios are 20:80 and 35:65 respectively. The styrene to ethylene-ethylene/propylene (S:EB-EP) ratios of Kuraray's SEPTON 4045 (SEEPS), 4055 (SEEPS), and 4077 (SEEPS) are typically about 37.6, 30, 30 respectively. More typically the (S:EB-EP) and (S:EP) ratios can vary broadly much like S:EB ratios of S-EB-S and ~~(SEB)_n~~ (SEB)_n from less than 19:81 to higher than 51:49 (as recited above) are possible. It should be noted that multiblock copolymers including SEPTON 4045 (SEEPS), 4055 (SEEPS), 4077 (SEEPS) and the like are described in my cited copending parent applications and are the subject matter of related inventions.

The block copolymers (II) such as Kraton G 1654X having ratios of 31:69 or higher can be used and do exhibit about the same physical properties in many respects to Kraton G 1651 while Kraton G 1654X with ratios below 31:69 may also be use, but they are less advantageous due to their decrease in the desirable properties of the final gel.

Plasticizers (III) particularly advantageous for use in practicing the present invention are will known in the art, they include rubber processing oils such as

paraffinic and naphthenic petroleum oils, highly refined aromatic-free paraffinic and naphthenic food and technical grade white petroleum mineral oils, and synthetic liquid oligomers of polybutene, polypropene, polyterpene, etc. The synthetic series process oils are high viscosity oligomers which are permanently fluid liquid nonolefins, isoparaffins or paraffins of moderate to high molecular weight.

Examples of representative commercially available plasticizing oils include Amoco® polybutenes, hydrogenated polybutenes, polybutenes with epoxide functionality at one end of the polybutene polymer, liquid poly(ethylene/butylene), liquid hetero-telechelic polymers of poly(ethylene/butylene/styrene) with epoxidized polyisoprene and poly(ethylene/butylene) with epoxidized polyisoprene: Example of such polybutenes include: L-14 (320 Mn), L-50 (420 Mn), L-100 (460 Mn), H-15 (560 Mn), H-25 (610 Mn), H-35 (660 Mn), H-50 (750 Mn), H-100 (920 Mn), H-300 (1290 Mn), L-14E (27-37 cst @ ~~100°F~~ 100°F Viscosity), H-300E (635-690 cst @ ~~210°F~~ 210°F Viscosity), Actipol E6 (365 Mn), E16 (973 Mn), E23 (1433 Mn), Kraton L-2203 and Kraton L-1203, EKP-206, EKP-207, HPVM-2203 and the like. Example of various commercially oils include: ARCO Prime (55, 70, 90, 200, 350, 400 and the like), Duraprime and Tufflo oils (6006, 6016, 6016M, 6026, 6036, 6056, 6206, etc) , other white mineral oils include: Bayol, Bernol, American, Blandol, Drakeol, Ervol, Gloria, Kaydol, Litetek, Lyondell (Duraprime 55, 70, 90, 200, 350, 400, etc), Marcol, Parol, Peneteck, Primol, Protol, Sontex, Witco brand white oils including RR-654-P and the like. Generally, plasticizing oils with average molecular weights less than about 200 and greater than about 700 may also be used (e.g., H-300 (1290 Mn)).

Comparisons of oil extended S-EB-S triblock copolymers have been described in Shell Chemical Company Technical Bulletin SC:1102-89 (April 1989) "KRATON® THERMOPLASTIC RUBBERS IN OIL GELS" which is incorporated herein by reference.

The crystal gels can be made non-adhearing, non-sticking, (non-tacky), by incorporating an advantage amount of stearic acid (octadecanoic acid), metal stearates (e.g., calcium stearate, magnesium stearate, zinc stearate, etc.), polyethylene glycol distearate, polypropylene glycol ester or fatty acid, and polytetramethylene oxide glycol distearate, waxes, stearic acid and waxes, metal stearate and waxes, metal stearate and stearic acid. The use of stearic acid alone do not reduce tack. The amount of stearic acid is also important. As an example, ratio of 200 grams stearic acid to 2,000 gram of S-EB-S (a ratio of 0.1) will result in spotted tack reduction on the surface of the gel. A ratio of 250 to 2,000 will result in spotted crystallized stearic acid regions on the surface of the gel or spotted tack reduction. A ratio of 300 to 2,000 will result in complete tack reduction with large stearic acid crystallized regions on the surface of the gel.

When microcrystalline waxes are incorporated together with stearic acid, the crystallization of stearic acid completely disappears from the surface of the gel. For example excellent result is achieved with 200 grams of stearic acid, 150 grams of microcrystalline wax and 2,000 grams of S-EB-S. The same excellent result is achieved when S-EB-S is adjusted to 3,000 grams, 4,000 grams, etc. The same result is achieved with (I) copolymers as well as in combination with polymers (II) such as SEPS, S-EB-EP-S, ~~(S-EB-EP)_n~~, ~~(SEB)_n~~, ~~(SEP)_n~~, (S-EB-EP)_n, (SEB)_n, (SEP)_n polymers.

The crystal gels can also contain useful amounts of conventionally employed additives such as stabilizers, antioxidants, antiblocking agents, colorants, fragrances, flame retardants, flavors, other polymers in minor amounts and the like to an extent not affecting or substantially decreasing the desired properties. Additives useful in the crystal gel of the present invention include: tetrakis[methylene 3, -(3'5'-di-tertbutyl-4"-hydroxyphenyl) propionate] methane, octadecyl 3-(3",5"-di-tert-butyl-4"-hydroxyphenyl) propionate, distearyl-pentaerythritol-dipropionate, thiodiethylene bis-(3,5-ter-butyl-4-hydroxy) hydrocinnamate, (1,3,5-trimethyl-2,4,6-tris[3,5-di-tert-butyl-4-hydroxybenzyl] benzene), 4,4"-methylenebis(2,6-di-tert-butylphenol), ~~stearic~~ stearic acid, oleic acid, stearamide, behenamide, oleamide, erucamide, N,N"-ethylenebisstearamide, N,N"-ethylenebisoleamide, sterryl erucamide, erucyl erucamide, oleyl palmitamide, stearyl stearamide, erucyl stearamide, calcium stearate, other metal sterates, waxes (e.g., polyethylene, polypropylene, microcrystalline, carnauba, paraffin, montan, candelilla, beeswax, ozokerite, ceresine, and the like), teflon (TFE, PTFE, PEA, FEP, etc), polysiloxane, etc. The crystal gel can also contain metallic pigments (aluminum and brass flakes), TiO₂, mica, fluorescent dyes and pigments, phosphorescent pigments, aluminatetrihydrate, antimony oxide, iron oxides (Fe₃O₄, - ~~Fe₂O₃~~ Fe₂O₃, etc.), iron cobalt oxides, chromium dioxide, iron, barium ferrite, strontium ferrite and other magnetic particle materials, molybdenum, silicones, silicone fluids, lake pigments, aluminates, ceramic pigments, ironblues, ultramarines, phthalocynines, azo pigments, carbon blacks, silicon dioxide, silica, clay, feldspar, glass microspheres, barium ferrite, wollastonite and the like. The report of the committee on Magnetic Materials, Publication NMAB-426, National Academy Press (1985) is incorporated herein by reference.

The crystal gels can also be made into composites. The crystal gels can be casted unto various substrates, such as open cell materials, metals, ceramics, glasses, and plastics, elastomers, fluoropolymers, expanded fluoropolymers, Teflon (TFE, PTFE, PEA, FEP, etc), expanded Teflon, spongy expanded nylon, etc.; the molten crystal gel is deformed as it is being cooled. Useful open-cell plastics include: polyamides, polyimides, polyesters, polyisocyanurates, polyisocyanates,

polyurethanes, poly(vinyl alcohol), etc. Suitable open-celled Plastic (sponges) are described in "Expanded Plastics and Related Products", Chemical Technology Review No. 221, Noyes Data Corp., 1983, and "Applied Polymer Science", Organic Coatings and Plastic Chemistry, 1975. These publications are incorporated herein by reference.

The crystal gels denoted as "G" can be physically interlocked with a selected material denoted as "M" to form composites as denoted for simplicity by their combinations ~~G_nG_n, G_nG_nG_n, G_nM_n, G_nM_nG_n, M_nG_nM_n, M_nG_nG_n, G_nG_nM_n, M_nM_nM_nG_n, M_nM_nM_nG_nM_n, M_nG_nG_nM_n, G_nM_nG_nG_n, G_nM_nM_nG_n, G_nM_nM_nG_n, G_nG_nM_n M_n, G_nG_nM_n G_nM_n, G_nM_nG_nG_n, G_nG_nM_n, G_nM_nG_nM_nM_n, M_nG_nM_nG_nM_nG_n, G_nG_nM_nM_nG_n, G_nG_nM_nG_nM_nG_n G_nG_n, G_nG_nG_n, G_nM_n, G_nM_nG_n, M_nG_nM_n, M_nG_nG_n, G_nG_nM_n, M_nM_nM_nG_n, M_nM_nM_nG_nM_n, M_nG_nG_nM_n, G_nM_nG_nG_n, G_nM_nM_nG_n, G_nM_nM_nG_n, G_nG_nM_n M_n, G_nG_nM_n G_nM_n, G_nM_nG_nG_n, G_nG_nM_n, G_nM_nG_nM_nM_n, M_nG_nM_nG_nM_nG_n, G_nG_nM_nM_nG_n G_nG_nM_nG_nM_nG_n, and the like or any of their permutations of one or more G_n with M_n, and the like or any of their permutations of one or more G_n with M_n and the like, wherein when n is a subscript of M, n is the same or different selected from the group consisting of paper, foam, plastic, fabric, metal, concrete, wood, glass, ceramics, synthetic resin, synthetic fibers or refractory materials and the like; wherein when n is a subscript of G, n denotes the same or a different gel rigidity of from about 2 gram to about 1,800 gram Bloom). The crystal gels of the composites are formed from copolymers (I), polymers (II), and plasticizers (III) described above.~~

Sandwiches of crystal gel-material (i.e., crystal gel-material- crystal gel or material-crystal gel-material, etc.) are useful as dental floss, shock absorbers, acoustical isolators, vibration dampers, vibration isolators, and wrappers. For example the vibration isolators can be use under research microscopes, office equipment, tables, and the like to remove background vibrations. The tear resistance nature of the instant crystal gels are superior in performance to amorphous block copolymer gels which are much less resistance to crack propagation caused by long term continue dynamic loadings.

The crystal gels are prepared by blending together the components including other ~~additives~~ additives as desired at about ~~230°C~~ 230°C to about ~~400°C~~ 100°C forming a paste like mixture and further heating said mixture uniformly to about ~~150°C~~ 150°C to about ~~200°C~~ 200°C until a homogeneous molten blend is obtained. Lower and higher temperatures can also be utilized depending on the viscosity of the oils and amounts of multiblock copolymers (I) and polymer (II) used. These components blend easily in the melt and a heated vessel equipped with a stirrer is all that is required. Small batches can be easily blended in a test tube using a glass stirring rod for mixing. While conventional large vessels with pressure

and/or vacuum means can be utilized in forming large batches of the instant crystal gels in amounts of about 40 lbs or less to 10,000 lbs or more. For example, in a large vessel, inert gases can be employed for removing the composition from a closed vessel at the end of mixing and a partial vacuum can be applied to remove any entrapped bubbles. Stirring rates utilized for large batches can range from about less than 10 rpm to about 40 rpm or higher.

The crystal gel articles can be formed by blending, injection molding, extruding, spinning, casting, dipping and other conventional methods. For example, Shapes having various cross-section can be extruded. The crystal gels can also be formed directly into articles or remelted in any suitable hot melt applicator and extruded into shaped articles and films or spun into threads, strips, bands, yarns, or other shapes. With respect to various shapes and yarn, its size are conventionally measured in denier (grams/9000 meter), tex (grams/1000 meter), and gage (1/2.54 cm). Gage, tex, denier can be converted as follows: tex = denier/9 = specific gravity (2135/gage), for rectangular cross section, tex = specific gravity (5806 X 10³)(th)(w)/9, where th is the thickness and w the width of the strip, both in centimeters. General descriptions of (1) block copolymers, (2) elastomeric fibers and conventional (3) gels are found in volume 2, starting at pp. 324-415, volume 6, pp 733-755, and volume 7, pp. 515 of ENCYCLOPEDIA OF POLYMER SCIENCE AND ENGINEERING, 1987 which volumes are incorporated herein by reference.

The crystal gels are excellent for cast molding and the molded products have various excellent characteristics which cannot be anticipated from the properties of the raw components. Other conventional methods of forming the composition can be utilized.

Not only do the crystal gels have all the desirable combination of physical and mechanical properties substantially similar to high viscosity amorphous S-EB-S gels such as high elongation at break of at least 1,600%, ultimate tensile strength of about 8X10⁵ dyne/cm² and higher, low elongation set at break of substantially not greater than about 2%, substantially about 100% snap back when extended to 1,200% elongation, and a gel rigidity of substantially from about 2 gram to about 1,800 gram Bloom and higher, the crystal gels of the present invention exhibit improved tear resistance and resistance to fatigue not obtainable from amorphous S-EB-S gels at corresponding gel rigidities.

The crystal gels of the present invention exhibit one or more of the following properties. These are: (1) tensile strength of about ~~8X10⁵ dyne/cm²~~ 8X10⁵ dyne/cm² to about ~~10⁷ dyne/cm²~~ 10⁷ dyne/cm² and greater; (2) elongation of less than about 1,600% to about 3,000% and higher; (3) elasticity modules of about ~~10⁴ dyne/cm²~~ 10⁴ dyne/cm² to about ~~10⁶ dyne/cm²~~ 10⁶ dyne/cm² and greater; (4) shear modules of about

~~104 dyne/cm²~~ 104 dyne/cm² to about ~~106 dyne/cm²~~ 106 dyne/cm² and greater as measured with a 1, 2, and 3 kilogram load at ~~23°C~~ 23°C; (5) gel rigidity of about less than about 2 gram Bloom to about 1,800 gram Bloom and higher as measured by the gram weight required to depress a gel a distance of 4 mm with a piston having a cross-sectional area of 1 square cm at ~~23°C~~ 23°C; (6) tear propagation resistance greater than the tear resistance of amorphous S-EB-S gels at corresponding gel rigidities; (7) resistance to fatigue greater than the fatigue resistance of amorphous S-EB-S gels at corresponding gel rigidities; (8) and substantially 100% snap back recovery when extended at a crosshead separation speed of 25 cm/minute to 1,200% at ~~23°C~~ 23°C. Properties (1), (2), (3), and (6) above are measured at a crosshead separation speed of 25 cm/minute at ~~23°C~~ 23°C.

The crystal gel articles molded from the instant crystal gels have additional important advantages in that they end-use performance properties are greater than amorphous S-EB-S gels in that they are more resistant to cracking, tearing, crazing or rupture in flexural, tension, compression, or other deforming conditions of use. Like amorphous gels, the molded articles made from the instant composition possess the intrinsic properties of elastic memory enabling the articles to recover and retain its original molded shape after many extreme deformation cycles.

Because of their improved tear resistance and improved resistance to fatigue, the crystal gels of the present invention achieve greater performance than amorphous gels in low frequency vibration applications, such as viscoelastic layers in constrained-layer damping of mechanical structures and goods, as viscoelastic layers used in laminates for isolation of acoustical and mechanical noise, as anti-vibration elastic support for transporting shock sensitive loads, as vibration isolators for an optical table, as viscoelastic layers used in wrappings, enclosures and linings to control sound, as compositions for use in shock and dielectric encapsulation of optical, electrical, and electronic components.

Because of their improved tear resistance and improved resistance to fatigue, the crystal gels are more useful as molded shape articles for use in medical and sport health care, such use include therapeutic hand exercising grips, dental floss, crutch cushions, cervical pillows, bed wedge pillows, leg rest, neck cushion, mattress, bed pads, elbow padding, dermal pads, wheelchair cushions, helmet liner, cold and hot packs, exercise weight belts, traction pads and belts, cushions for splints, slings, and braces (for the hand, wrist, finger, forearm, knee, leg, clavicle, shoulder, foot, ankle, neck, back, rib, etc.), and also soles for orthopedic shoes. Other uses include various shaped articles as toys, optical uses (e.g., cladding for cushioning optical fibers from bending stresses) and various optical devices, as lint removers, dental floss, as tips for swabs, as fishing bate,

as a high vacuum seal (against atmosphere pressure) which contains a useful amount of a mineral oil-based magnetic fluid particles, etc. Moreover, the casted, extruded, or spun threads, strips, yarns, tapes can be weaved into cloths, fine or coarse fabrics.

The crystal gels can be formed in any shape; the original shape can be deformed into another shape (to contact a regular or irregular surface) by pressure and upon removal of the applied pressure, the composition in the deformed shape will recover back to its original shape.

As an example of the versatility of use of the instant crystal gels, a hand exerciser can be made in any shape so long as it is suitable for use as a hand exerciser: a sphere shape, a cube shape, a rectangular shape, etc. Likewise, a wheelchair cushion can be made from the composition in any shape, so long as it meets the needs of the user of the cushion. For example, a cushion can be made by forming the composition into a selected shape matching the contours of the specific body part or body region. The composition can be formed into any desired shaped, size and thickness suitable as a cushion; the shaped composition can be additionally surrounded with film, fabric, foam, or any other desired material or combinations thereof. Moreover, the composition can be casted onto such materials, provided such materials substantially maintain their integrity (shape, appearance, texture, etc.) during the casting process. The same applies for brace cushions, liners, linings and protective coverings for the hand, wrist, finger, forearm, knee, leg, etc.

Because of their improved tear resistance and resistance to fatigue, the crystal gels exhibit versatility as balloons for medical uses, such as balloon for valvuloplasty of the mitral valve, gastrointestinal balloon dilator, esophageal balloon dilator, dilating balloon catheter use in coronary angiogram and the like. Since the crystal gels are more tear resistant, they are especially useful for making condoms, toy balloons, and surgical and examination gloves. As toy balloons, the crystal gels are safer because it will not rupture or explode when punctured as would latex balloons which often times cause injuries or death to children by choking from pieces of latex rubber. The crystal gels are advantageously useful for making gloves, thin gloves for surgery and examination and thicker gloves for vibration damping which prevents damage to blood capillaries in the fingers and hand caused by handling strong shock and vibrating equipment.

Other uses include self sealing enclosures for splicing electrical and telephone cables and wires. For example, the crystal gels can be pre-formed into a small diameter tubing within an outer elastic tubing, both the internal crystal gel tubing and external elastic tubing can be axially expanded and fixed in place by a removable continuous retainer. Upon insertion of a spliced pair or bundle of cables

or wires, the retainer can be removed, as the retainer is removed, the crystal gel and elastic tubing impinges onto the inserted cables or wires splices, thereby sealing the electrical splices against weather, water, dirt, corrosives and shielding the splice from external abuse. The enclosure is completed without the use of heat or flame as is conventionally performed.

The crystal gels of the invention can be formed into gel strands, gel tapes, gel sheets, and other articles of manufacture. Moreover, because of their improved resistance to tearing, the crystal gels do not tear as readily as amorphous gels when used as dental floss. The dental floss can be almost any shape so long as it is suitable for dental flossing. A thick shaped piece of the composition can be stretched into a thin shape and used for flossing. A thinner shaped piece would require less stretching, etc. For purposes of dental flossing, while flossing between two closely adjacent teeth, especially between two adjacent teeth with substantial contact points and more especially between two adjacent teeth with substantial amalgam alloy metal contact points showing no gap between the teeth, it is critical that the crystal gel resist tearing, shearing, and crazing while being stretched to a high degree in such situations. For example, dental crystal gel floss can take the form of a disk where the segments of the circumference of the disk is stretched for flossing between the teeth. Other shaped articles suitable for flossing include threads, strips, yarns, tapes, etc., mentioned above.

In order for crystal gels to be useful as a dental floss, it must overcome the difficult barriers of high shearing and high tearing under extreme elongation and tension loads. The difficulties that the crystal gels must overcome during flossing can be viewed as follows: during the action of flossing, the crystal gel is stretched from no less than about 200% to about 1,100% or higher, the crystal gel floss is deformed as it is pulled down with tearing action between the contacting surfaces of the teeth, then, the wedge of crystal gel floss is sheared between the inner contacting surfaces of the teeth, and finally, the elongated wedged of crystal gel floss is pulled upwards and out between the surfaces of the teeth. The forces encountered in the act of flossing are: tension, shearing, tearing under extreme tension.

The use of crystal gels advances the flossing art by providing strong, soft, and more tear resistant gels than amorphous gels. Floss made from the crystal gels has many advantages over conventional dental floss such as regular and extra fine waxed and unwaxed nylon floss, spongy nylon fiber floss, and waxed and unwaxed expanded and unexpanded teflon floss. Such conventional floss are not recommended for use by children, since a slip or sudden snap in forcing the floss between the teeth may cause injury to the gums which often times results in bleeding. For

sensitive gums and inflamed gums which has become red and puffy, it is difficult to floss at, near, and below the gumline. The soft crystal gel floss with softness substantially matching the softness of the gums are of great advantage for use by children and for flossing teeth surrounded by sensitive and tender gums.

In all cases, the tear strength of crystal gels are higher than that of amorphous gels. The rigidities of the crystal gels for use as dental floss advantageously should be selected to exhibit a propagating tear force (when propagating a tear as measured at ~~180°~~ 180° U bend around a 5.0 mm diameter mandrel attached to a spring scale) of at least about 1 Kg/cm, more advantageously at least 2 Kg/cm, and still more advantageously of about 3 Kg/cm and higher. For any gel to be considered useful for flossing, the gels should exhibit tear strengths of at least 2 Kg/cm and higher, advantageously of at least 4 Kg/cm and higher, more advantageously of at least 6 Kg/cm and higher, exceptionally more advantageously of at least 8 Kg/cm and higher. Typically, the tear propagation strength should range from about 5 Kg/cm to about 20 Kg/cm and higher, more typically from about less than 5 Kg/cm to about 25 Kg/cm and higher, especially more typically from about less than 6 Kg/cm to about 30 Kg/cm and higher, and exceptionally more typically from about less than 8 Kg/cm to about 35 Kg/cm and higher.

For any gel to be considered useful for flossing, the gels, critically, should advantageously exhibit a propagating tension tear force (when a cylindrical sample is notched and a tear is initiated at the notched area and propagated past its maximum cylindrical diameter by length-wise stretching of the cylindrical sample) of at least about 1 Kg/cm, more advantageously at least 2 Kg/cm, and still more advantageously of about 4 Kg/cm and higher. Although the crystal gels of the present invention have improved tear resistance and resistance to fatigue greater than the amorphous gels at corresponding gel rigidities, the high and ultra-high tear resistant gels of my other related parent and c-i-p applications typically will exhibit even higher tear resistance values.

The crystal gels of the invention find use as airbags designed for rapid deployment by expanding pressurized or ignitable gas as shown in Figs 1a-9i, 10d, 10e, 12, and 15.

The various components are denoted by:

1 Shape of gel expansion envelop. 2 Gel, 3 External retainer, 5 internal retainer, 6 reinforcing retainer, 7 mechanical retainer, 8 semi integral retainer, 9 integral pin retainer, 10 partial external integral retainer, 12 body, 13 gas inlet from ~~filter~~ filter, 14 outer sheet, 15 inner sheet, 16 eye retainer ring cavity, 18, back partial integral retainer, 19 T retainer (integral reinforcing), 20 thin gel ~~diaphragm~~ diaphragm, 21 thick gel ~~diaphragm~~ diaphragm, 22 multiple ~~progressive~~

~~progressive thinner thinner~~ gel ~~diaphragm~~ diaphragm, 23 multiple ~~prograssive~~ progressive ~~thicher~~ thicker gel ~~diagraphm~~ diaphragm, 24 multiple single layer expansion control elements, 25 ~~single~~ single layer expansion control elements, 26 dual single layer expansion control elements, 27 ~~multiple~~ multiple layer expansion control elements, 28 multiple layer diverted elements, 29 patterned MDE, 31 full retained gel cup, 32 partial retained gel cup, 33 gel cavity, 34 S gel shaped, 35 bulged gel, 36 compact assembly, 37 double layered, 38 multiple window, 39 ~~double~~ double gel, 40 baffle, 41 gel dia., 42 expanded 7a-7d, 43 non-uniform gel dia., 44 gel restrainer, 45 ~~restained~~ restrained envelope, 46 non-uniform gel expanded mass, 47 expansion retainer assembly, 48 expansion control elements, 50 dual ~~expansion~~ expansion dia., 52 ~~single~~ single, 54 internal and external, 56 triple, 57 multiple layered, 58 triple internal, 59 triple small and dural large, 60 equal triple, 61 dural internal with single external surround dia., 10c driver gel dia., 10d enveloping driver dummy, 10e ~~eveloping~~ enveloping ~~passenger~~ passenger dummy, 11 ~~convential~~ conventional air bag deployment, 12 ge and break-out pressures, 13 gel diameter expansion final pressures.

The expansion of the gel air bag is substantially pure volume expansion or dilation as related to K, bulk modulus, y , young's modulus: $K=y/3(1-2t)$, $t=3k-2n/6k-2n$, where t =poisson's ratio, $b=1/k$ compressibility = -change in $V/(V \cdot$ change in pressure $P)$.

Surface expansion measure of air bag from initial to expanded state is from 630 to 833% depending on thickness of original air bag. The ~~initail~~ initial air bag thickness can vary from .5 cm to 10 cms. (.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 cm and higher).

While advantageous components and formulation ranges based on the desired properties of the crystal gels have been disclosed herein. Persons of skill in the art can extend these ranges using appropriate material according to the principles discussed herein. All such variations and deviations which rely on the teachings through which the present invention has advanced the art are considered to be within the spirit and scope of the present invention.

The invention is further illustrated by means of the following illustrative embodiments, which are given for purpose of illustration only and are not meant to limit the invention to the particular components and amounts disclosed.

EXAMPLE I

Gels of 100 parts of high viscosity linear Kraton G1651 (amorphous S-EB-S), Septon 8006 (amorphous S-EB-S), and a high viscosity radial amorphous midblock segment (SEB) n triblock copolymers and 1,600, 1,200, 1,000, 800, 600, 500, 450, 300,

250 parts by weight of Duraprime 200 white oil (plasticizer) are melt blended and samples molded, the bulk gel rigidities are found to be within the range of 2 to 1,800 gram Bloom and the tensile strength, notched tear strength, and resistance to fatigue are found to decrease with increase amounts of plasticizers.

EXAMPLE II

Example I is repeated using high viscosity crystalline midblock segment linear S-EB-S and radial (SEB)_n triblock copolymers with ethylene to butylene midblock ratios (E:B) of 89:11, 88:12, 87:13, 86:14, 85:15, 84:16, 83:17, 82:18, 81:19, 80:20, 79:21, 78:22, 77:23, 76:24, 75:25, 74:26, 73:27, 72:28, 71:29, and 70:30 in combination with an equal amount of amorphous S-EB-S having (E:B) ratio of about 60:40, the bulk gel rigidities are found to be within the range of 2 gram to 1,800 gram Bloom and the notched tear strength and resistance to fatigue of the gel at corresponding rigidities are found to be greater than that of amorphous gels of Example I.

EXAMPLE III

Gels of 100 parts of Kraton G1651 (amorphous S-EB-S), Septon 8006 (amorphous S-EB-S), and a high viscosity amorphous midblock segment (SEB)_n linear and radial triblock copolymers, 1,600, 1,200, 1,000, 800, 600, 500, 450, 300, 250 parts by weight of Duraprime 200 white oil (plasticizer), and 10 parts of Dow polydimethylsiloxane are melt blended and samples molded, the bulk gel rigidities are found to be within the range of 2 to 1,800 gram Bloom and the tensile strength, notched tear strength, and resistance to fatigue are found to decrease with increase amounts of plasticizers.

EXAMPLE IV

Gels of 100 parts of Kraton G1651 (amorphous S-EB-S), Septon 8006 (amorphous S-EB-S), and a high viscosity amorphous midblock segment (SEB)_n linear and radial triblock copolymers, 1,600, 1,200, 1,000, 800, 600, 500, 450, 300, 250 parts by weight of Duraprime 200 white oil (plasticizer), and 2 parts of Dupont Teflon AF 1600 are melt blended and samples molded, the bulk gel rigidities are found to be within the range of 2 to 1,800 gram Bloom and the tensile strength, notched tear strength, and resistance to fatigue are found to decrease with increase amounts of plasticizers.

EXAMPLE V

Example III is repeated using high viscosity crystalline midblock segment linear S-EB-S and radial (SEB)_n triblock copolymers with ethylene to butylene

midblock ratios (E:B) of 89:11, 88:12, 87:13, 86:14, 85:15, 84:16, 83:17, 82:18, 81:19, 80:20, 79:21, 78:22, 77:23, 76:24, 75:25, 74:26, 73:27, 72:28, 71:29, and 70:30 in combination with an equal amount of amorphous S-EB-S having (E:B) ratio of about 60:40, the bulk gel rigidities are found to be within the range of 2 gram to 1,800 gram Bloom and the notched tear strength and resistance to fatigue of the gel at corresponding rigidities are found to be greater than that of amorphous gels of Example III.

EXAMPLE VI

Example IV is repeated using high viscosity crystalline midblock segment linear S-EB-S and radial (SEB)_n triblock copolymers with ethylene to butylene midblock ratios (E:B) of 89:11, 88:12, 87:13, 86:14, 85:15, 84:16, 83:17, 82:18, 81:19, 80:20, 79:21, 78:22, 77:23, 76:24, 75:25, 74:26, 73:27, 72:28, 71:29, and 70:30 in combination with an equal amount of amorphous S-EB-S having (E:B) ratio of about 60:40, the bulk gel rigidities are found to be within the range of 2 gram to 1,800 gram Bloom and the notched tear strength and resistance to fatigue of the gel at corresponding rigidities are found to be greater than that of amorphous gels of Example IV.

EXAMPLE VII

Gels of 100 parts of high viscosity linear (S-EB-S), (S-EP-S), (S-B-EP-S), (S-B-EB-S), (S-B-EP-B-S), (S-B-EB-B-S), (S-B-EB-EP-S), (S-B-EP-EB-S), (S-EB-EP-S), (S-EP-B-EP-S), (S-B-EB-B-EB-S), (S-B-EB-B-EP-S) and (S-B-EP-B-EP-B-S) block copolymers and 1,600, 1,200, 1,000, 800, 600, 500, 450, 300, 250 parts by weight of Duraprime 200 white oil (plasticizer) are each melt blended and samples molded, the bulk gel rigidities are found to be within the range of 2 to 1,800 gram Bloom and the tensile strength, notched tear strength, and resistance to fatigue are found to decrease with increase amounts of plasticizers.

EXAMPLE VIII

Gels of 100 parts of high viscosity linear (S-EB₄₅-EP-S), ~~(S-E-EB₂₅-S)~~ (S-E-EB₂₅-S), (S-EP-E-EP-S), (S-E-EB-S), (S-E-EP-S), (S-E-EP-E-S), (S-E-EB-B-S), (S-E-B-EB-S), (S-E-B-EP-S), (S-E-EB-EP-S), (S-E-EP-EB-S), (S-E-EP-E-EP-S), (S-E-EP-E-EB-S), (S-E-EB-B-EP-S), (S-E-EP-B-EB-S), (S-E-EP-E-EP-E-S), (S-E-EP-E-EB-S), (S-E-EP-E-EP-EB-S), (S-E-EP-E-EP-E-S), and (S-E-EP-EB-EP-EB-B-S) block copolymers and 1,600, 1,200, 1,000, 800, 600, 500, 450, 300, 250 parts by weight of Duraprime 200 white oil (plasticizer) are each melt blended and samples molded, the bulk gel rigidities are found to be within the range of 2 to 1,800 gram Bloom and the tensile strength, notched tear strength, and resistance to fatigue are found to be greater than that of amorphous gels of Example VII.

EXAMPLE IX

Example VIII is repeated and minor amounts of 2, 5, 10 and 15 parts of the following polymers are formulated with each of the triblock copolymers: styrene-butadiene-styrene block copolymers, styrene-isoprene-styrene block copolymers, low viscosity styrene-ethylene-butylene-styrene block copolymers, styrene-ethylene-propylene block copolymers, styrene-ethylene-propylene-styrene block copolymers, styrene-butadiene, styrene-isoprene, polyethyleneoxide, poly(dimethylphenylene oxide), polystyrene, polybutylene, polyethylene, polypropylene, high ethylene content EPDM, amorphous copolymers based on 2,2-bistrifluoromethyl-4,5-difluoro-1,3-dioxole/tetrafluoroethylene. The bulk gel rigidities of each of the formulations are found to be within the range of 2 gram to 2,000 gram Bloom and the notched tear strength and resistance to fatigue of the gels at corresponding rigidities are found to be greater than that of amorphous gels of Example I formulated with corresponding amounts of the same polymers.

EXAMPLE X

Molten gels of Examples I-IX are formed into composites with paper, foam, plastic, elastomers, fabric, metal, concrete, wood, glass, ceramics, synthetic resin, synthetic fibers, and refractory materials and the resistance to fatigue of the composite-crystal gels at corresponding rigidities are found to be greater than that of the composite-amorphous gels.

EXAMPLE XI

Three cm thick sheets of each of the crystal gels of Example II and VIII and the amorphous gels of Example I and VII are tested by repeatedly displacing the sheets to a depth of 1 cm using a 10 cm diameter smooth (water soaked) wood plunger for 1,000, 5,000, 10,000, 25,000, 50,000, and 100,000 cycles. The sheets of crystal gels are found capable of exhibiting greater fatigue resistance than the sheets of amorphous gels at corresponding rigidities.

While preferred components and formulation ranges have been disclosed herein persons of skill in the art can extend these ranges using appropriate material according to the principles discussed herein. Furthermore, Crystalline midblock segment block polymers can be use in blending with other engineering plastics and elastomeric polymers to make alloyed compositions having improved impact and tear resistance properties. All such variations and deviations which rely on the teachings through which the present invention has advanced the art are considered to be within the spirit and scope of the present invention.

ABSTRACT

Novel crystal gels and articles are formed from one or more block copolymers having at least one crystalline midblock and high levels of a plasticizer, said midblock segment of at least one copolymer having an amount of crystallinity sufficient to achieve improvements in one or more physical properties including improved crack propagation resistance, improved tear resistance, improved resistance to fatigue and resistance to catastrophic failure not obtainable in amorphous gels.

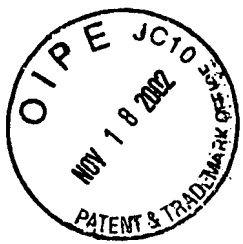


Fig. 5c



Fig. 5d

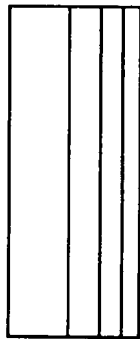


Fig. 5e



Fig. 5f



Fig. 5g

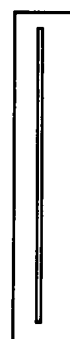


Fig. 5h



Fig. 5i



Fig. 5j



Fig. 5k

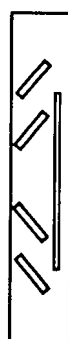


Fig. 5l



Fig. 5m

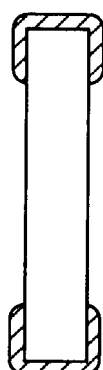


Fig. 5n



Fig. 5o



Fig. 5p

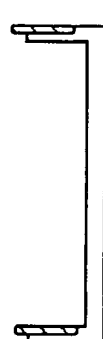


Fig. 5q



Fig. 5r

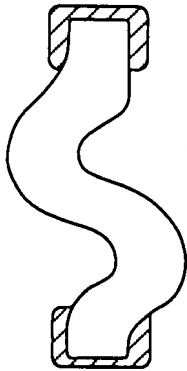


Fig. 5s



Fig. 5t



Fig. 5u



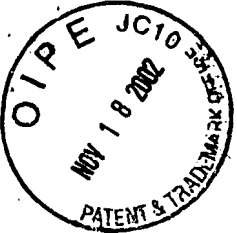
~~Fig. 5v~~
5v



~~Fig. 5w~~
5w



~~Fig. 5x~~
5x



1875-1880

